

# From Starch and Sugar

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Starches and sugars belong to the important group of substances known as carbohydrates. Because they are an essential part of all plants, carbohydrates occur everywhere and in a supply that is replaced each year.

The name of the group comes from the simplest formula,  $\text{CH}_2\text{O}$ , for the central compound, D-glucose—or dextrose, as it is known commercially. D-Glucose contains only carbon, hydrogen, and oxygen. In most of the principal members of the group, hydrogen and oxygen occur in the same ratio as in water. In fact, the French, who did the early research in this field, named the group *hydrate de carbone* (hydrate of carbon). The Germans translated it as *Kohlenhydrate*, and in English it became *carbohydrate*.

Dextrose, or D-glucose, is outstanding among the carbohydrates, both chemically and biologically. It is the product of photosynthesis in the green leaves of plants in the presence of sunlight. In the process, the raw materials are carbon dioxide and water; oxygen is formed as a byproduct. The energy of the sun is stored in green leaves in this way.

Sucrose, the sugar that is obtained from sugarcane and sugar beets, is made up of one unit of glucose and one unit of fructose. These two simpler sugars differ only in the structural arrangement of their atoms. Sucrose is found in the sap of nearly all plants

and is stored in fairly high concentration in the sugar beet.

Glucose is the fundamental unit of two other important plant materials, cellulose and starch, which differ only in the structural arrangement of the glucose units. Cellulose is a structural building material of plants. Starch is the form in which carbohydrates are stored in many plants. It occurs as small granules, which are rather easily separated in pure form from the rest of the plant.

MANY OF THE INDUSTRIAL USES of starch as such are based on its physical characteristics: It can form a thick paste in water, and it is a white, finely divided, and free-flowing powder that can be incorporated in foodstuffs. Its most important chemical characteristics are that it may be broken down into simpler units and that it is a polyhydroxy alcohol. Starch may be broken down into its simplest unit, D-glucose, by acid or enzyme hydrolysis. By reaction with suitable chemical reagents, such as acid anhydrides or alkyl halides, it is possible to prepare, from starch, ester and ether derivatives, the properties of which differ greatly from those of the raw material itself although the size of the starch molecule is essentially retained. If the substitution is limited, the product, like starch itself, is insoluble in organic solvents but dispersible in water. More completely substituted starch derivatives, on the other hand, are usually more soluble in organic solvents and less soluble in water.

In 1948 more than 8 million pounds of cornstarch was used by the explosives industry, part as a nonexplosive ingredient in fireworks and dynamite, but much of it, after nitration, as an explosive agent. These starch nitrates, or nitrostarches as they are sometimes less correctly called, are esters formed

by the reaction of nitric acid with starch in the presence of either sulfuric acid or phosphoric acid as a catalyst. The use of phosphoric acid leads to starch nitrates, which are more stable than those obtained with sulfuric acid.

Starch phosphate, another ester of starch with an inorganic acid, also has interesting and valuable properties. When phosphorus oxychloride is allowed to react with starch granules in the presence of pyridine, which is an organic base, approximately one hydroxyl group in each of the repeating units of the starch molecule can be converted to a phosphate ester. This starch monophosphate, insoluble in hot or cold water and in organic solvents, and containing strongly acidic groups, has valuable ion-exchange properties. That is, the compounds can be used to soften water or to remove the metallic ion of many inorganic salts from solutions containing them—a desirable procedure in such industrial processes as the demineralization of sugar sirups. The nature of the starch phosphate obtained under similar conditions of reaction is greatly influenced by the variety of starch used. The starches with smaller granules show the greatest reactivity with the phosphorylating reagent.

Starch normally swells in hot water to form a paste. Water-resistant starches that are completely unaffected by boiling water, or even by heating above the boiling point in an autoclave, can be prepared by treating starch with appropriate chemical reagents. Organic diisocyanates, such as hexamethylene diisocyanate, react with starch in the presence of pyridine to form cross links, or bridges, between the carbohydrate chains. These cross-linked products are notably inert, and may find uses as dusting powders, insecticide carriers, or fillers for plastics. Treatment of starch under suitable conditions with such other reagents as formaldehyde, glyoxal, dibasic acid chlorides, or phosphorus oxychloride can also convert it to products that swell little if at all under conditions

that completely gelatinize untreated starch.

Acetates of whole starch or of each of its fractions may be prepared by treatment with acetic acid-acetic anhydride mixtures in the presence of catalysts. The acetates of whole starch or of amylopectin are too brittle and weak to form fibers or plastics. But the amylose triacetate (and other saturated aliphatic triesters) can be formed into cellophanelike films, which are lustrous and pliable. Amylose triacetate can also be converted into fibers resembling acetate rayon by a process known as dry spinning, in which a viscous chloroform solution of the amylose triacetate is forced through tiny holes of a spinneret into a hot-air chamber for evaporation of the solvent. The resulting threads are wound on a reel. Mixed acetyl with higher acyl radicals (such as the mixed acetate-propionate of amylose) are thermoplastic and can be molded into plastic articles. More extensive use of the valuable properties of the amylose derivatives depends on economic factors.

Other esters of starch (such as the propionate, benzoate, xanthate, palmitate, thiocyanate, sulfate, and chloride esters) and ethers (such as the methyl, ethyl, and benzyl derivatives) have been prepared. Many of these are being investigated with a view to possible industrial use.

Of particular importance are esters of the starch-containing unsaturated groups. Starch methacrylate can readily be polymerized to form insoluble materials, and may thus be of value as a plastic or as a coating compound.

An interesting compound is obtained by the reaction of chloroacetic acid with starch in the presence of sodium hydroxide. The product, called carboxymethyl starch, is said to be a potential replacement material for various natural gums in foods, cosmetic preparations, pharmaceuticals, and some other products where a stable thickening agent, constant in properties from batch to batch, is required.

The allyl ether of starch, another im-

portant unsaturated derivative, is prepared by heating starch, a strong alkali solution, and allyl chloride in a closed vessel. The ether formed is a doughy material, which dissolves readily in organic solvents. Sprayed or painted on surfaces, the solutions form a film that dries tack-free in a short time. On exposure to air, the material behaves like a drying oil in that it takes up oxygen to form an insoluble hard resin. It is useful as a coating material, an adhesive, and an ingredient in printing inks. Sulfur may be substituted for oxygen in the polymerization process. Mixtures with sulfur may be used to form rigid plastics and laminates.

Allyl starch has been successfully tested for the following applications:

As surface coatings for furniture finishes, interior wood finishes, and metal finishes.

As bronzing liquid, thermosetting adhesive, overprint and finishing varnish, and printing-ink vehicle.

Other miscellaneous uses such as solventproofing paper and greaseproofing paper, fast-drying undercoats, plastic for wood and other laminates, leather dressing, synthetic enamels, and dope for aircraft finishes.

For each of those uses, proper formulation (addition of plasticizers, resins, driers) must be used.

Samples and limited commercial quantities of allyl starch are available.

Allyl sucrose (made from ordinary cane or beet sugar) has properties similar to those of allyl starch. Unlike allyl starch, allyl sucrose is compatible with drying oils.

Alkoxides of starch have been prepared in which a metallic atom or ion takes the place of a hydrogen atom on a hydroxyl group of the starch. Sodium starchate has been prepared by heating the starch in an organic solvent containing dissolved sodium hydroxide. Other metal derivatives have been prepared from the sodium derivative. The evidence indicates that only the hydroxyl on the second carbon atom of the anhydroglucose unit is attacked. The sodium atom may be replaced by

treatment with metal salts, alkyl halides, and other reagents. The copper derivative is a mildew-proofing agent. Other derivatives are being studied, and new uses are being sought for compounds prepared by use of the starch alkoxides as intermediates.

THUS FAR WE HAVE DISCUSSED the chemical products from starch in which little or no breakdown of the molecule has occurred. One possible product from the more drastic degradation of starch is *l*-glucosan, an anhydride of the beta form of glucose. When starch is heated to 350° C. in an evacuated system, 60 percent of the original weight distills over as a brown viscous sirup. Treating this distillate with boiling acetone gives crystalline *l*-glucosan, which, after recrystallization, is a white, alkali-stable, anhydro sugar that contains three hydroxyl groups. The crystalline material is neutral in reaction, free from unstable reducing substances, and stable to light and air. On acid hydrolysis, it is converted quantitatively to dextrose. The process for the preparation of *l*-glucosan from starch has received considerable study in the research laboratory. Because no expensive chemicals need be used in the degradation, but only heat and simultaneous distillation under reduced pressure, economical production will probably be possible if suitable uses are found for it or its derivatives.

The cleavage of starch, dextrose, or sorbitol by hydrogen at high temperatures and pressures in the presence of a suitable catalyst, such as finely divided nickel, results in their conversion in good yield to a mixture of propylene glycol, ethylene glycol, and glycerol. In times of national emergency when our supply of glycerol from natural fats is inadequate, the process may have particular significance. In Germany during the Second World War, a mixture of glycols and glycerol, obtained by the hydrogenolysis of carbohydrates and called "glycerogen," was marketed as an antifreeze and for other purposes.

Levulinic acid, a 5-carbon  $\gamma$ -keto

acid, has been prepared industrially by heating dextrose-containing materials or starch in aqueous solutions of mineral acids. It is used pharmaceutically in the form of its calcium salt and has promise as a chemical intermediate for use in plastics and in the synthesis of other organic chemicals.

We have discussed a number of chemical products from starch, but the subject is by no means exhausted. A host of other products—such as acetone, butyl alcohol, 2,3-butylene glycol, lactic acid, citric acid, and ethyl alcohol—result from the fermentation of carbohydrate substrates. Many further uses are being explored, and other new starch compounds are being made for examination of their properties and industrial utilization whenever possible. Now let us consider the sugars.

A NUMBER OF SUGARS are actually and potentially available for use as chemical raw materials.

Dextrose is manufactured from cornstarch in pure form in the United States to the extent of more than 600 million pounds annually. The same product can be obtained from other starches. In northern Europe, where little corn is grown, it is usually prepared from potato starch.

Dextrose also has been prepared from wheat starch in this country in recent years to supplement that available from cornstarch.

Sucrose is produced in quantity from sugarcane and sugar beets.

Maltose is potentially available in large quantities from starch by hydrolysis with enzymes.

Lactose is the sugar from milk.

Raffinose may be obtained as a by-product in the manufacture of sucrose from sugar beets.

Xylose, or wood sugar, can be obtained in large quantities from crop residues. It is the sugar from which comes most of the furfural, an important industrial chemical, when agricultural residues are treated with hot dilute acid.

Arabinose, from which furfural can

also be obtained, occurs in combined form in various plant polysaccharides.

Galactose can be obtained from lactose by hydrolysis.

Fructose, or fruit sugar, can be derived from sucrose by hydrolysis. It can also be obtained from inulin from the Jerusalem artichoke and other inulin-bearing plants, or it can be prepared chemically by the action of a mild alkaline catalyst on dextrose.

THOSE SUGARS the chemist divides into two classes—reducing and nonreducing. Sucrose and raffinose are nonreducing sugars; they do not reduce copper and silver salts under certain conditions. Their chemical reactions are those of alcohols only, unless the molecules are broken down in some way. Both give reducing sugars on hydrolysis. The other sugars all have the property of reducing copper and silver salts under specified conditions.

The reducing sugars have another active group, besides the hydroxyl or alcohol groups of the nonreducing sugars. Because of the presence of this other active group, the reducing sugars are capable of forming a class of compounds known as glycosides. The corresponding derivatives of glucose or dextrose are termed glucosides.

THE GLYCOSIDES as a class are important biologically. Living organisms often render toxic materials harmless by converting them to glycosides. The essential principles in a number of pharmaceutical preparations are glycosides. Digitalis is one of the cardiac glycosides that stimulate the heart. Rutin, obtained on a commercial scale from buckwheat, is a flavanol glycoside. Another flavanol glycoside, hesperidin, was formerly thought to be identical with "vitamin P." Natural dye materials often are glycosides; indican, from which indigo was formerly obtained, is an example. Streptomycin, an important antibiotic, is a glycoside of a previously unknown disaccharide.

The glycosides we have mentioned are obtained from natural sources, al-

though they can be prepared by synthesis. Glycosides of higher alcohols can be prepared; they are nonionic surface-active substances and may be used as emulsifiers. The solubility of these materials in water is improved by treatment with materials like ethylene oxide. The formation of a glycoside may be used to increase the water solubility of a pharmaceutical preparation—for example, the glycosides of 2-alkyl-1,4-naphtho-hydroquinone, an antihemorrhagic agent. Sometimes the action is changed by such treatment. The glucoside of sulfapyridine is reported to have appreciable activity against cholera, in contrast to sulfapyridine itself.

THE REDUCING SUGARS can be converted to the sugar alcohols by catalytic or electrolytic reduction processes. Then the reducing group is no longer present. For example, the hydrogenation of dextrose under neutral or acidic conditions yields principally the hexahydric alcohol sorbitol, which is a white, odorless, crystalline, water-soluble compound. Sorbitol is an established article of commerce used for its humectant or conditioning properties. It is a chemical intermediate in the manufacture of vitamin C; when it is esterified with fatty acids, it forms edible, nonionic emulsifying agents used in ice cream and other food products and in pharmaceutical preparations. Drying oils prepared from sorbitol esterified with long-chain unsaturated fatty acids are said to be rapid-drying and to give hard, alkali-resistant coatings. Fatty acid esters have been suggested as plasticizers for polyvinyl chlorides, polyvinyl chloride acetates, and polyvinyl butyrals. They have been recommended also as textile lubricants, and the monoesters as textile sizes. In many of its derivatives, sorbitol actually exists as an anhydride, sorbitan, resulting from the loss of water during derivative formation. Reduction of dextrose under alkaline conditions gives a mixture of sorbitol and mannitol, both hexahydroxy alcohols which differ only

in the spatial arrangement of their constituent atoms. Similar products are obtained from both. Nitrated mannitol is used as an explosive and in medicine as a vasodilator.

Xylitol is potentially available in large quantities, because it can be obtained by the hydrogenation of xylose. This pentitol (5-carbon sugar alcohol) would be expected to have properties similar to those of the hexitols (6-carbon sugar alcohols) mannitol and sorbitol. A rare pentitol, ribitol is one of the units in the structure of riboflavin, vitamin B<sub>2</sub>. This naturally occurring vitamin may be synthesized in several ways.

The polyols, or sugar alcohols, can be converted readily to their anhydrides by heating with catalytic amounts of strong mineral acids or other dehydrating agents. They are formed often during the preparation of their derivatives. The anhydrides as a class are reported to be humectants, particularly for tobacco, and softeners for papers and textiles. Isomannide, from mannitol, has been patented as a diuretic. Styrcitol, from mannitol, forms an explosive tetranitrate. The anhydride dinitrates show depressor action, similar to that of glycerol trinitrate and mannitol hexanitrate.

The oxidation of glucose, either electrolytically or by the action of hypohalites, gives gluconic acid; its nitric acid oxidation gives the dibasic saccharic acids. Other sugars give similar acids. Shorter-chain acids can be prepared by oxidation of dextrose under different conditions. Tartaric and oxalic acids can be obtained from glucose by oxidation with nitric acid in the presence of vanadium salts. Good yields are reported. Glucuronic acid, another valuable oxidation product of glucose, has received attention recently as a remedy for certain types of arthritis.

A NUMBER of ether and ester derivatives, like those prepared from starch, can be prepared from the sugars. The properties differ in some respects because of the great difference in mole-

ular size. The methacrylyl esters and allyl ethers of the sugars form insoluble resins on exposure to air in the same way as the corresponding compounds from starch. The allyl ethers of the sugars dissolve in a wider range of solvents than those of starch, but their coatings do not dry tack-free in a short time, as do those of starch, because the sugar ethers are liquids at ordinary temperatures. If the allyl ethers of the sugars are first blown with air, they dry much faster. Sucrose octa-acetate has been used in a special formula for denaturing alcohol, as a gum constituent of lacquers, as a plasticizer in anhydrous adhesives, and in the treatment of paper.

CERTAIN BODY STRUCTURES composed of lightweight atoms do not show up in X-ray pictures. If some heavy atom could be introduced into the structure in question, X-ray shadow pictures would be formed. Iodo derivatives of galactose and of methyl glucoside have been found useful as contrasting agents. These derivatives are rapidly excreted through the kidneys after intravenous injection and are present in sufficient concentration to render the kidney structure opaque to X-rays.

Vitamin C (L-xyloascorbic acid) is synthesized from sorbitol, which, as we mentioned before, is a sugar alcohol obtained from dextrose. Bacterial oxidation converts the sorbitol to the sugar sorbose, which is then oxidized to ascorbic acid by chemical means. Other ascorbic acids can be prepared, for example, D-araboascorbic acid, which has but one-twentieth the antiscorbutic activity of vitamin C. The compounds differ only in the relative arrangement in space of the groupings in the molecule. Fatty acid esters of ascorbic acids have been used to inhibit rancidity in fats. Ascorbic acids are used to prevent the darkening of fruits during canning or freezing.

Many chemicals have been prepared from sugars by fermentation. These are discussed elsewhere in this volume.

Mention will be made of one process on the border line between fermentation and the usual chemical modifications of carbohydrates. That is the process for making methanol, or wood alcohol, from the gases obtained as a byproduct in the fermentation to produce butyl alcohol and acetone. The mixture of gases consists almost entirely of 60 percent carbon dioxide and 40 percent hydrogen. They are combined under high pressure in the presence of a suitable catalyst to give methanol and water. Methanol is readily converted to formaldehyde, an important chemical in the plastics field.

FROM THE EXAMPLES given, it is apparent that the field of potential chemical uses for the starches and sugars is exceedingly great. Many other chemical reactions of carbohydrates are known. Lactic acid may be obtained in fair yields by treating carbohydrate materials with strong alkali. Ordinarily it is obtained by fermentation methods. Under conditions of high temperature, carbohydrates have been converted in the laboratory to products resembling oil and bituminous coal, which some chemists believe were formed naturally from the carbohydrate materials of plants in past geologic ages. Starches and sugars will become more important sources of chemicals as we learn more about their reactions and the products thereof.

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